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LATERAL DIFFUSION IN COATING SYSTEMS

Report Documentation Page

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REASON FOR RESEARCH

- "The total direct cost of corrosion was determined to be $279 billion per year, which is 3.2 percent of the U.S. gross domestic product (GDP). Indirect costs to the user (society costs) are conservatively estimated to be equal to the direct costs."[1]
- Pollution
  - Removed paint then repaint
    - Volatile organic compounds
    - Constituents of original paint (lead …)
  - Paint and corrosion products dissolved into environment
    - Chromates, organics, metal (alloying components)
- Safety

1. Federal Highway Administration (FHWA), Office of Infrastructure Research and Development, Report FHWA-RD-01-156, September 2001

IS DIFFUSION IMPORTANT TO CORROSION?

- Corrosion is an electrochemical reaction of metals with the liquid environment
- Why do we care about diffusion?
  - Corrosion requires electrical contact, electrolyte
  - Corrosive ion transport, Cl^-
  - Corrosion inhibitors (chromates)
  - Optimize drying cycles
  - Design better accelerated testing protocols
- What diffuses?
  - Oxygen, water, chromates and other soluble inhibitors
  - Residual solvent or hydrolysis products out
  - UV absorbers, free radicals, pollutants

DIFFUSION IS IMPORTANT FOR:

- Water and ion movement
  - Through coating
  - Around pigments, fillers and ion exchange
- Movement of corrosion inhibitors
- Across substrate-coating interface
- Through oxide layers

COATING AS A BARRIER

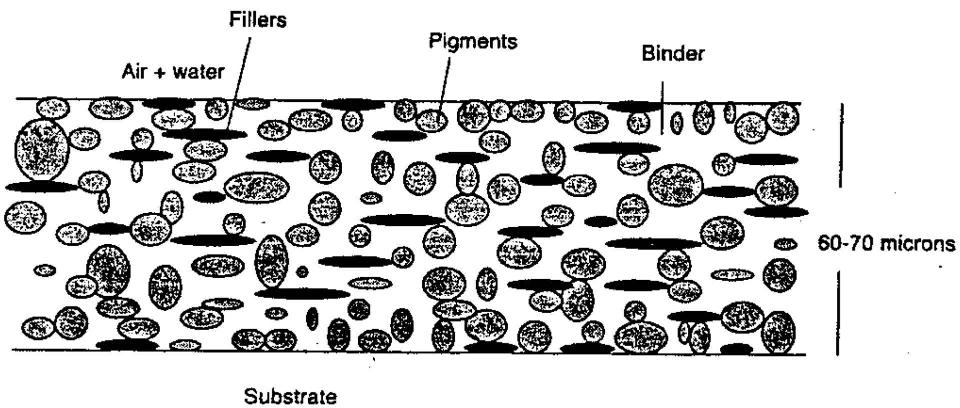


Figure 1. Sealing the underlying metal from contact with its corrosive environment, the barrier effect stops oxygen and water from penetrating down to the steel to create corrosion.

- Barriers, such as coatings, slow transport of water to substrate
  - Delay onset of corrosion
  - Bottleneck for corrosion progression
- Pigments and fillers make the diffusion path longer
- Ion exchange can remove environmental hazard en route
- Water acts as a conveyer for ions

Havard Undrum. (May 2006). Superior Protection. Coatings World, 43-48.

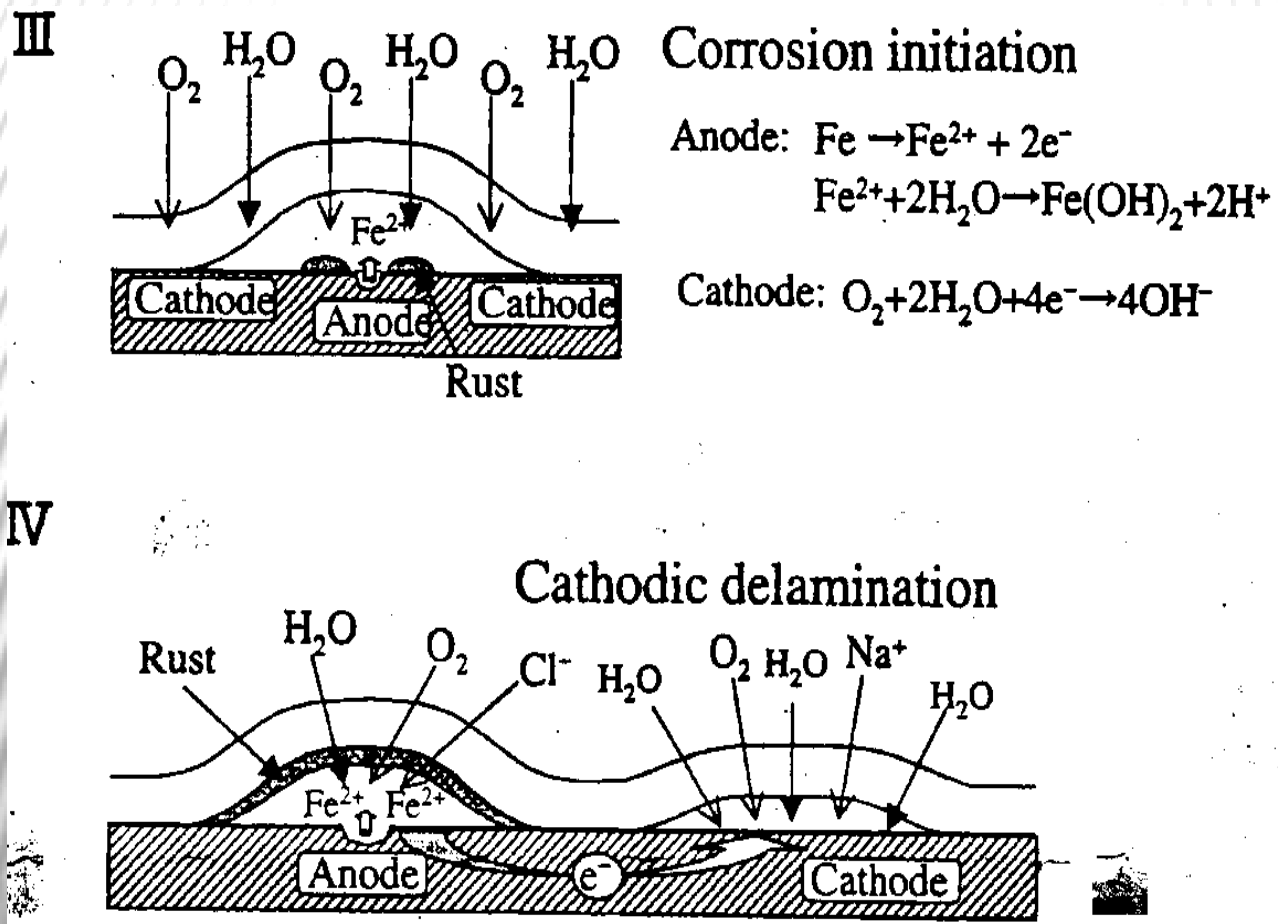
LATERAL DIFFUSION

- Water advance water along the substrate
- The advance of the water front includes a loss term as the water diffuses up through the topcoat

IMPACT OF LATERAL WATER DIFFUSION

- Hydrolysis of adhesion bonds
- Reaction with residual contaminants (Cl)
  - Osmotic pressure – blister formation
  - Corrosion catalyst
- Transport of active corrosion protectors

TRANSPORT AT COATING-SUBSTRATE INTERFACE



When corrosion begins, diffusion occurs in the plane of the coating. Diffusion is required to balance charge.

Often salt required to defeat metal oxide layer.

(LeChartlier principle)

J.H. Park, G. D., H. Ooshige, A. Nishikata, T. Tsuru. (2003). Monitoring of water uptake in organic coatings under cyclic wet-dry conditions. Corrosion Science, 45, 1881-1894.

CORROSION NEEDS CONTINUITY

183 5-8 Environmental Degradation of Materials

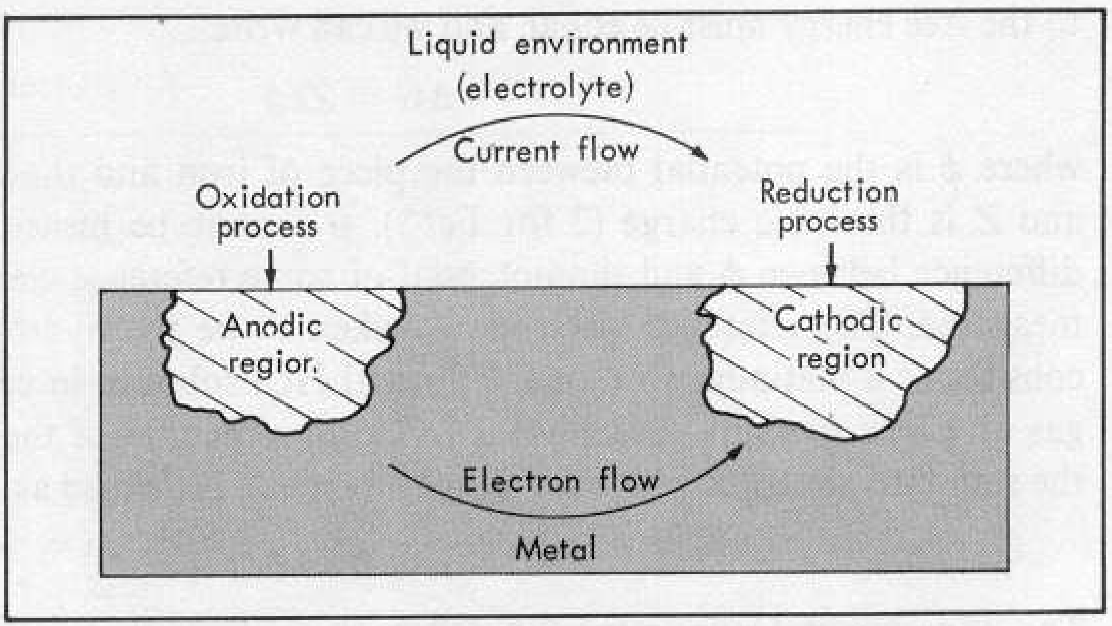


FIG. 5-30 Schematic illustration of metallic corrosion

Corrosion needs:

- Continuity between anode and cathode
- Focus on water movement

Craig R. Barrett, W. D.. (1973). The Principles of Engineering Materials. New Jersey: Prentice-Hall.

ASPECTS OF COATING SYSTEM THAT PROTECT

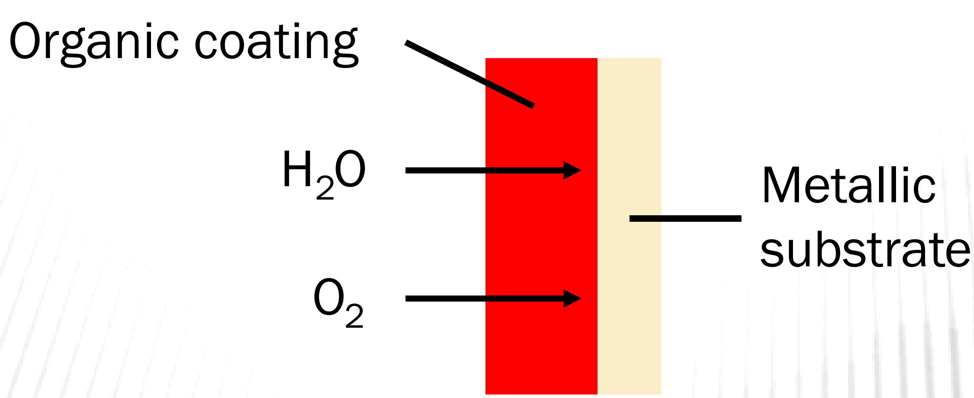
- Surface topography
  - Sanding
- Surface cleanliness
  - Chlorides and sulfides
  - Oils (protect metal, reduce adhesion)
- Pretreatment
- Primer
- Topcoat

TESTING METHODS FOR CORROSION PROTECTION

- Gloss
- Color
- Contact angle
- Visual indication of blister formation

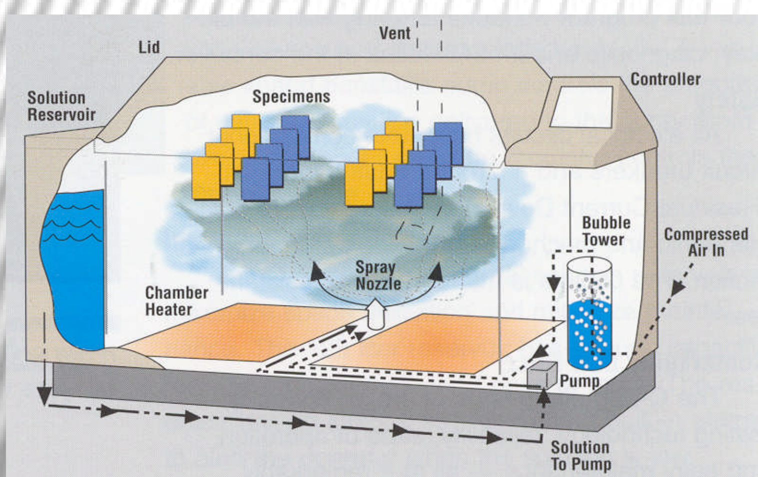
- Difficult to test pretreatment or surface treatment separately
  - Tracers
  - Indicators
  - EIS (traditional setup tests directly below cell)

ORGANIC BARRIER COATINGS

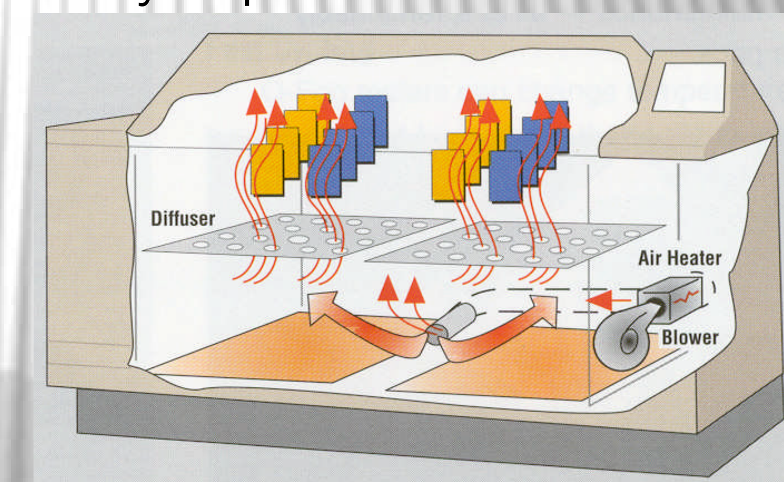


Prohesion test

Wet step



Dry step

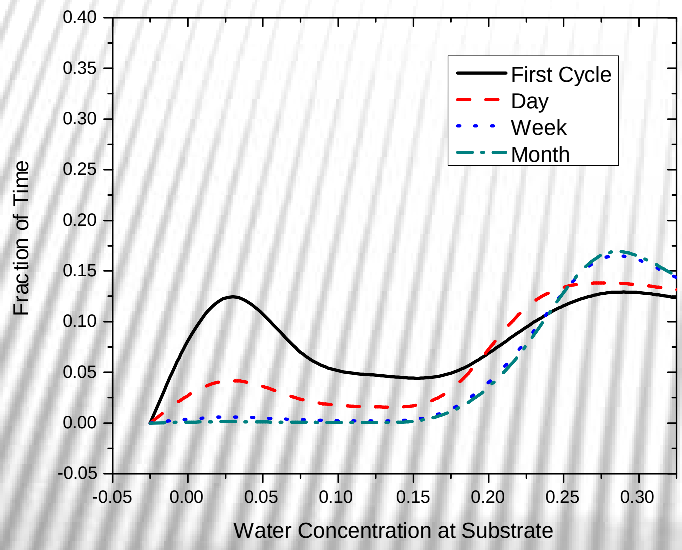


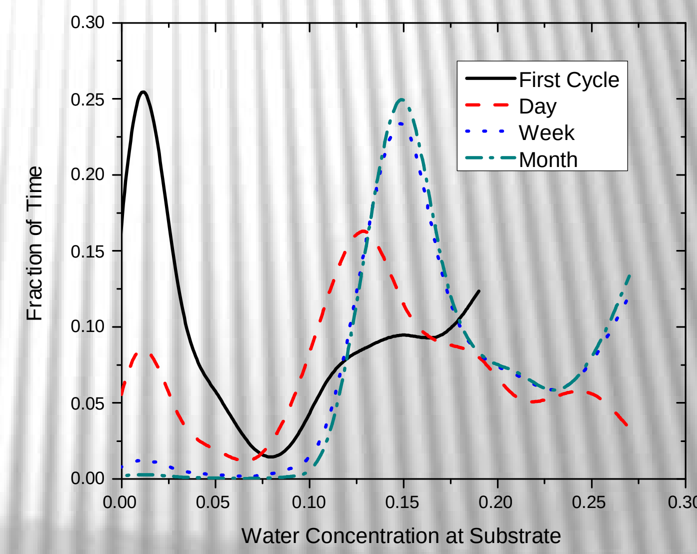
CYCLIC DIFFUSION

- Surface is exposed to water, then dry air
- Real-life and accelerated weathering
  - ASTM D5859
    - 1 week of:
      - 4 hours UV exposure at 60C
      - 4 hours of condensation at 50C
    - 1 week of:
      - 1 hour salt spray at 25C
      - 1 hour dry at 35C

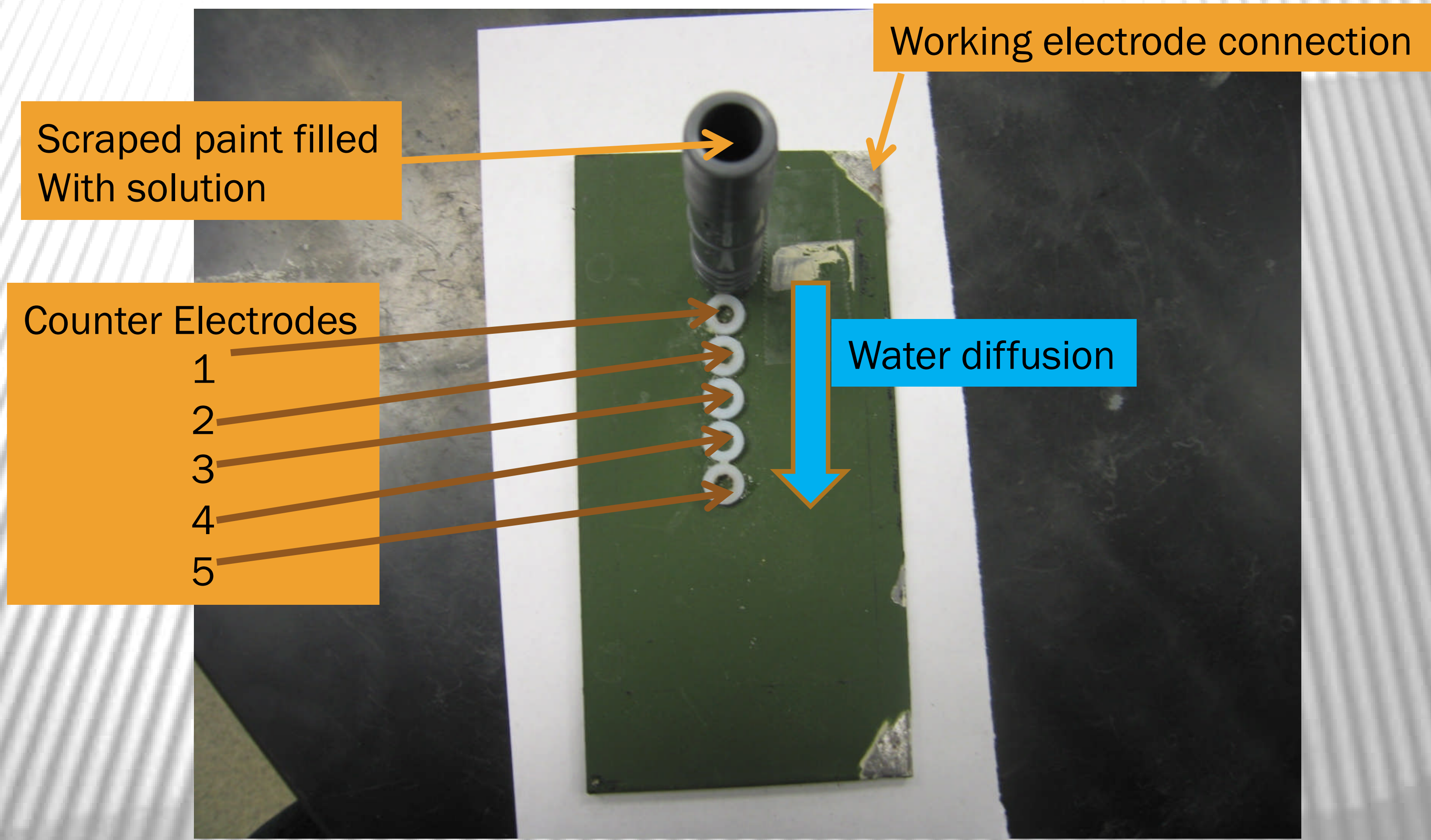
PHOTOCHEMICAL DEGRADATION (WATER AT SUBSTRATE)

- Average wet exposure duration
- Overall fraction of time exposed to water





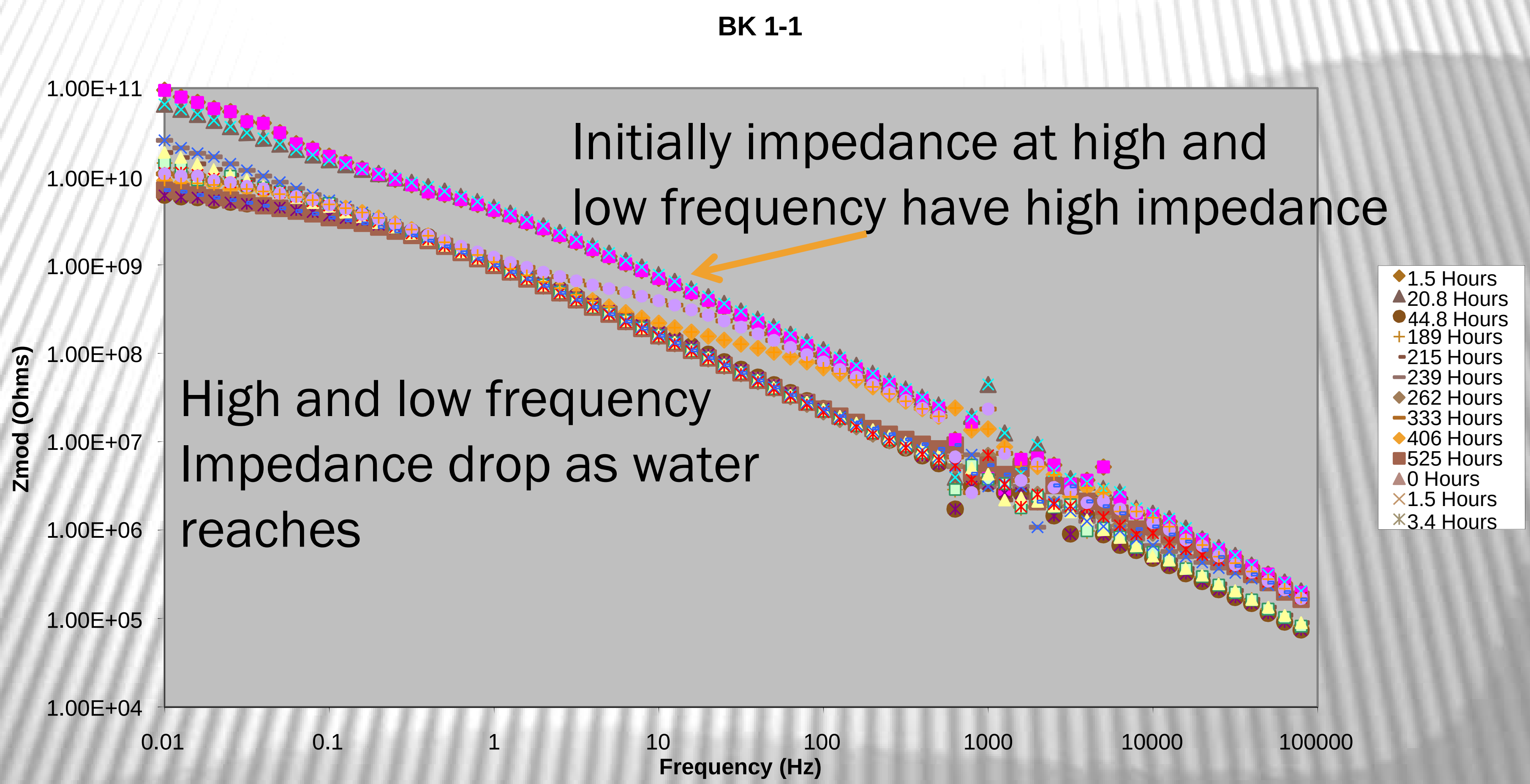
EXPERIMENTAL SETUP



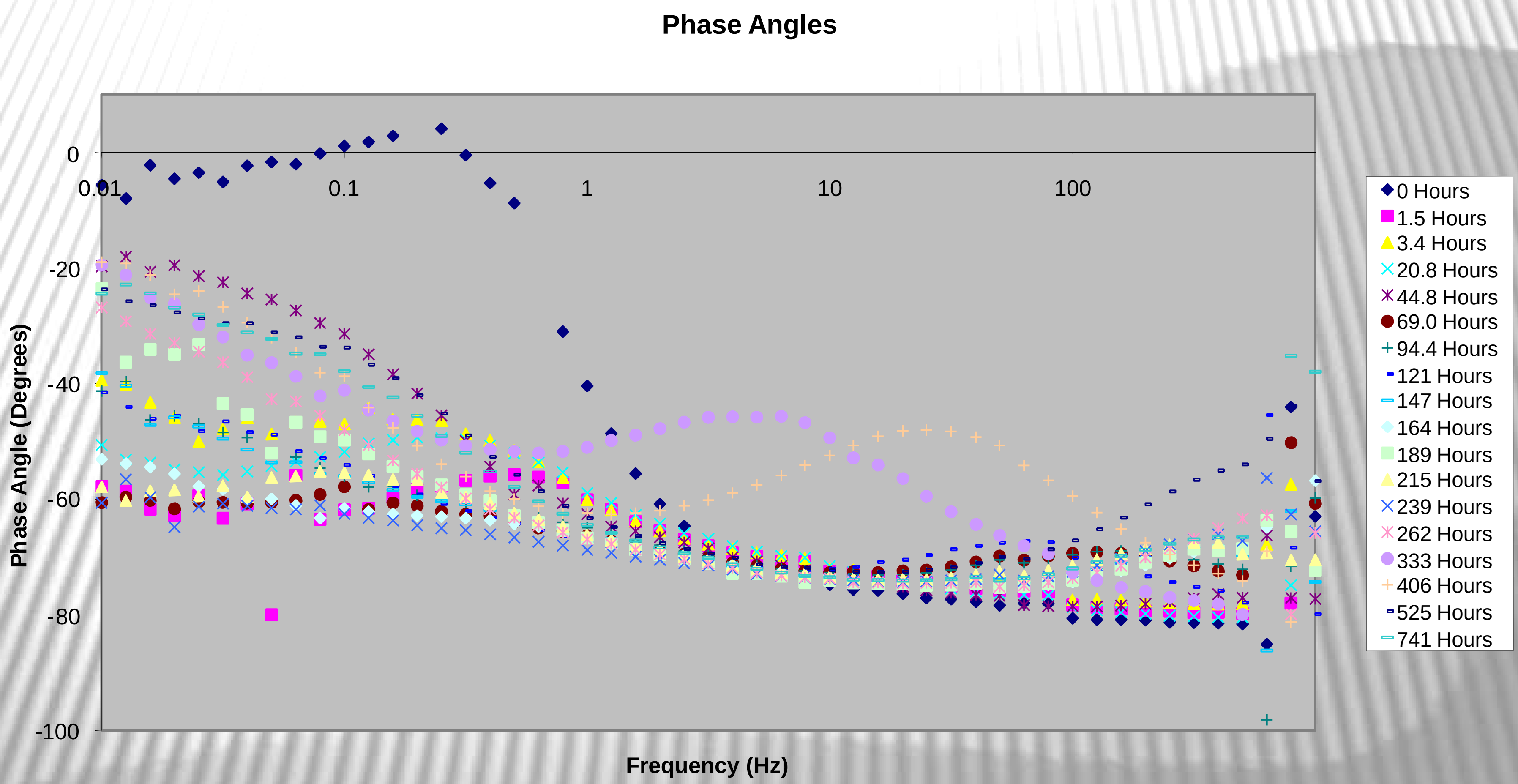
TEST

- Army Primer
- Army Topcoat
- Harrison solution
- Conducting Gels
- EIS spectra

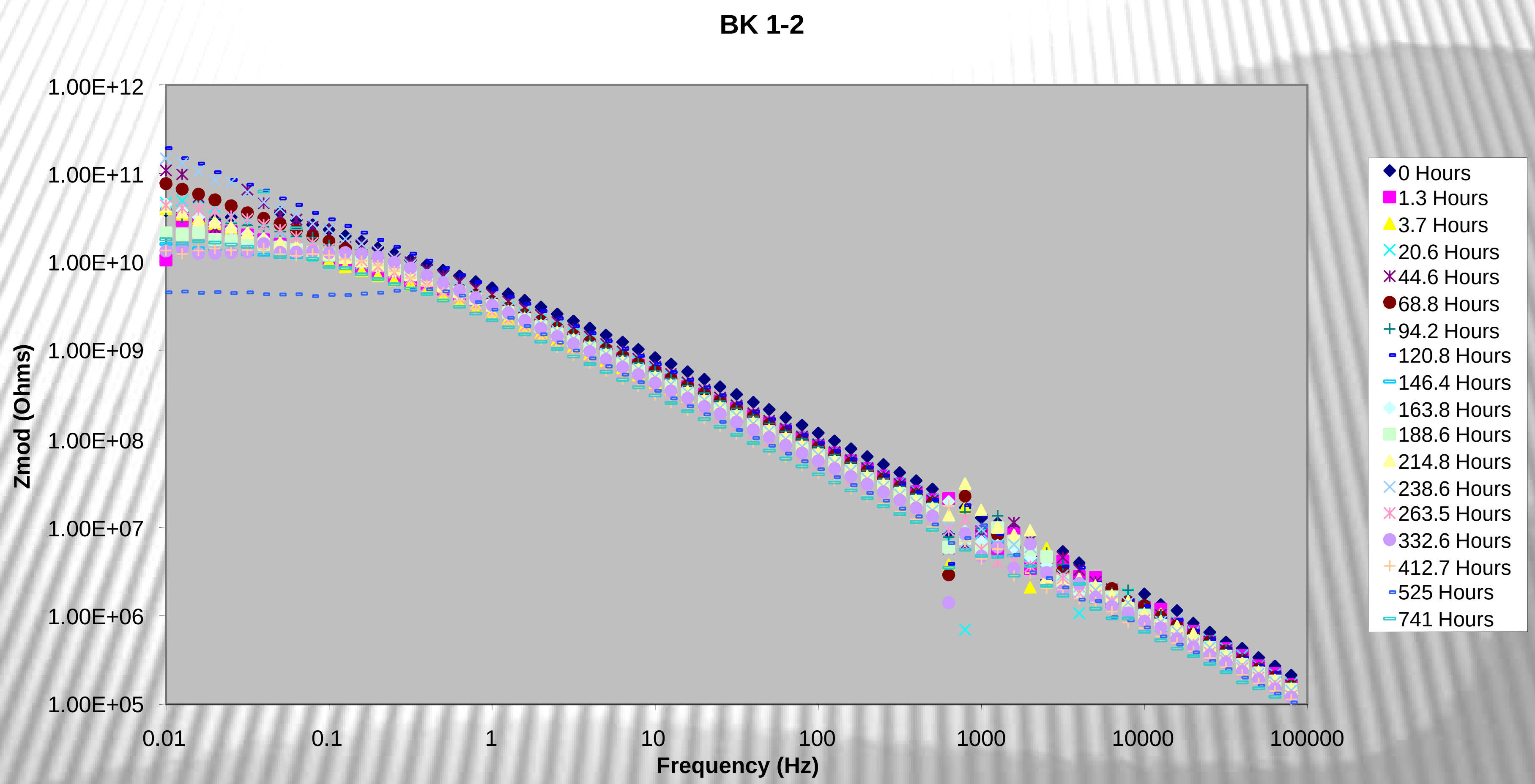
IMPEDANCE OF NEAREST CONTACT



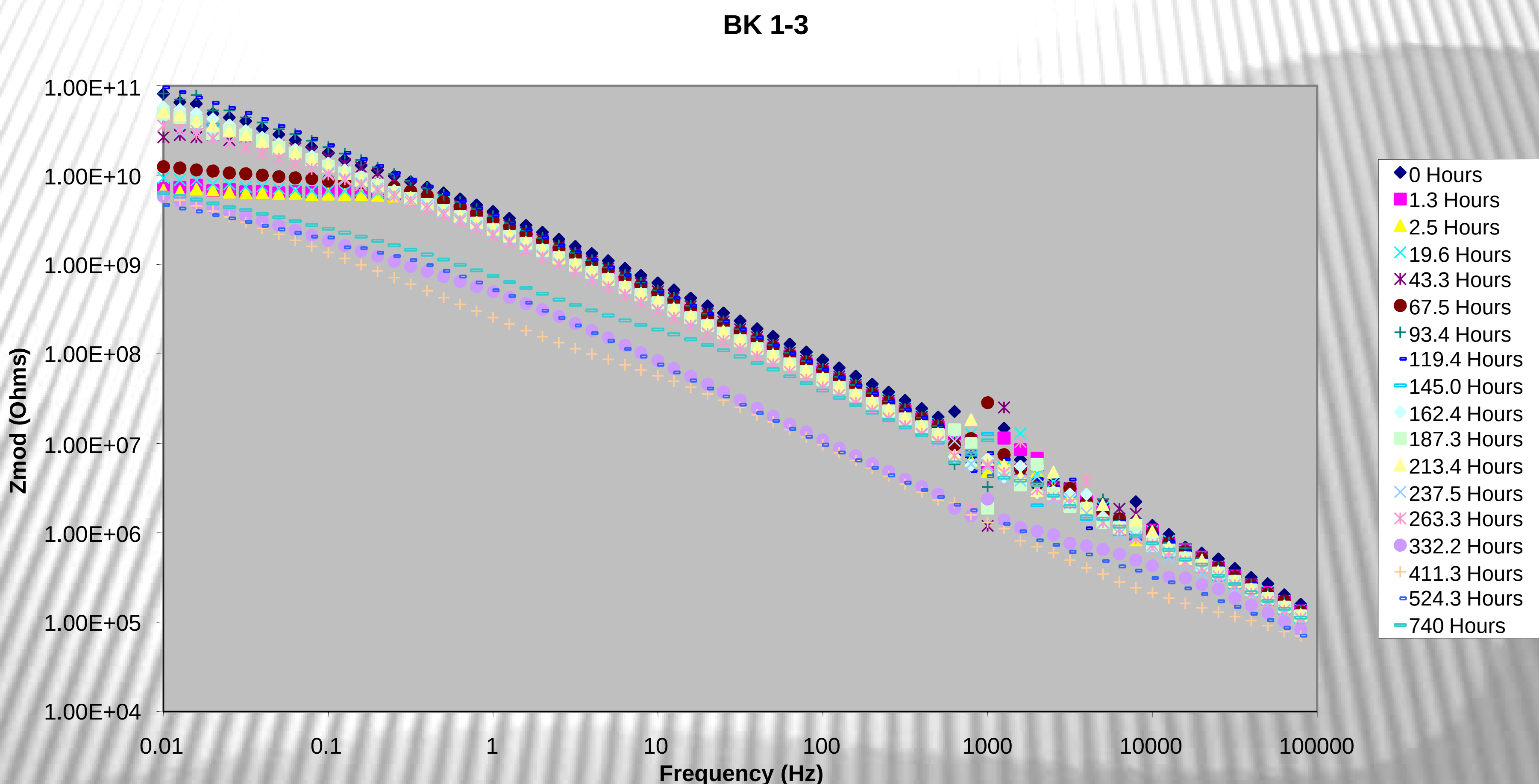
PHASE PLOT OF NEAREST CELL



IMPEDANCE TO SECOND CELL



IMPEDANCE TO 3RD CELL

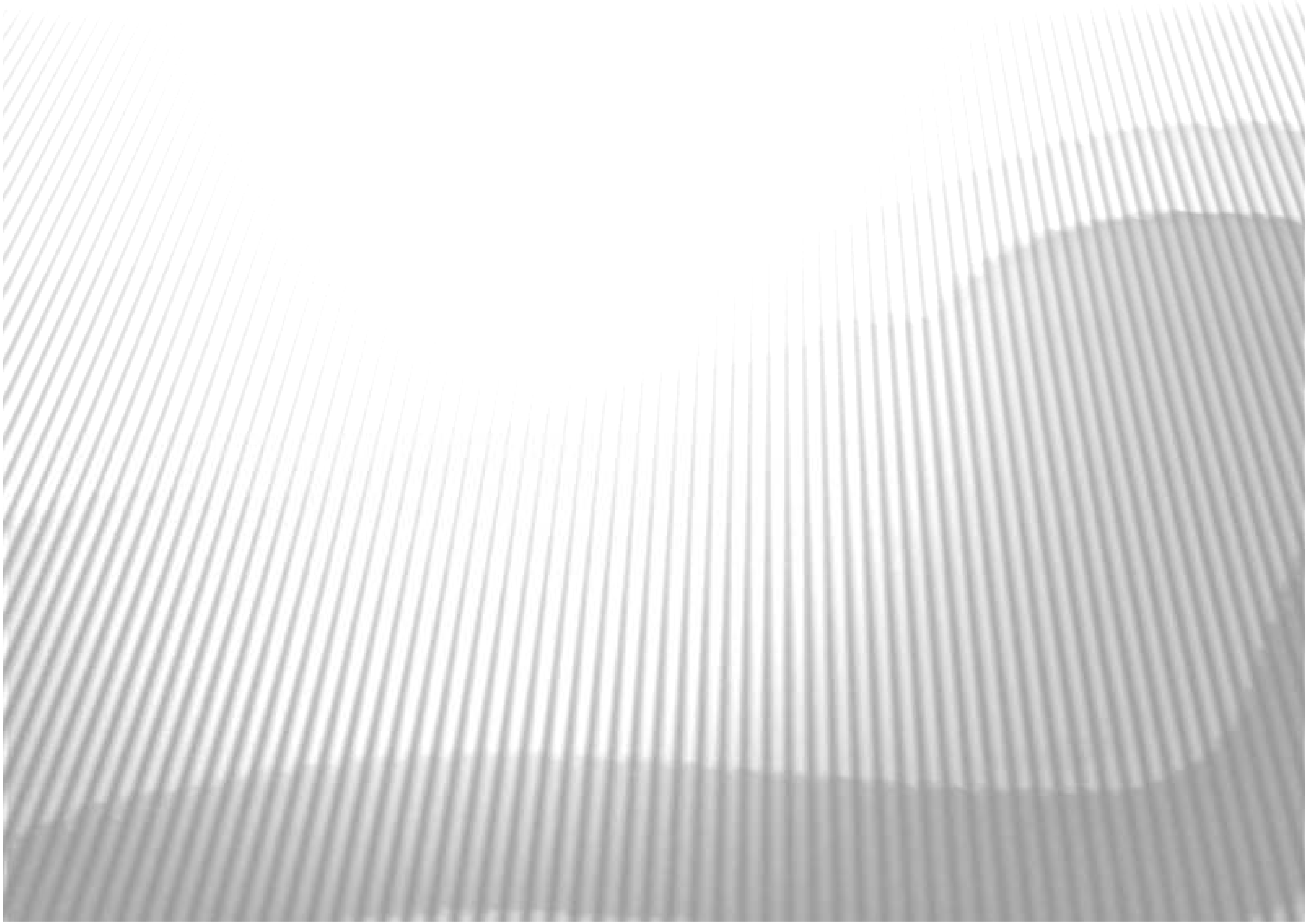


SUMMARY

- Lateral diffusion is being investigated to rank:
  - Surface preparations
  - Surface cleaning technologies
  - Pretreatments
- Testing is designed test complete systems

IMPACT OF LATERAL DIFFUSION

- Corrosion advance
  - Time to connect cathodic and anodic regions
- Concentration of the water needs to be sufficient for ion transport
  - Understand metal surface treatment, surface preparation, primer, topcoat (image thermal)



INTRODUCTION

- Accelerated weathering protocol
  - Need to test system designed to last for decades
- Reciprocity shown based on dose (Chin et. al. 2005)
  - But accelerated weathering protocols don't always match environmental exposures
- Simulations allow:
  - physical processes can be combined (UV absorption and diffusion)
  - Results to be quickly analyzed unambiguously
  - Experimental systems hard to design

COMPUTATIONAL TOOLS AND SELECT APPLICATIONS

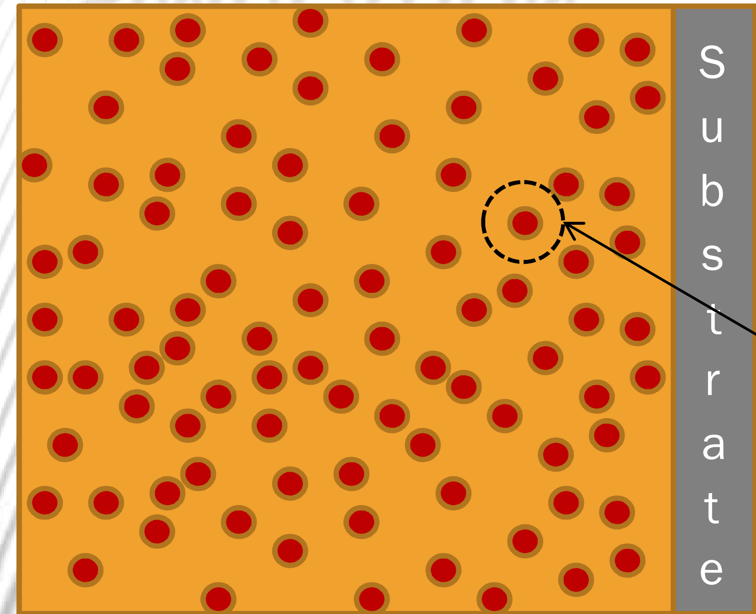
- Finite element analysis
  - Electromagnetic response (EIS and Dielectric spectroscopy)
  - Diffusion
  - Multiphysics (couple the above)
- Monte Carlo – Coating as a composite breakdown
- Finite difference – coupled photodegradation/ hydrolysis
- Molecular dynamics – simulate ion and water transport
- Quantum chemistry – polymer chain scission location

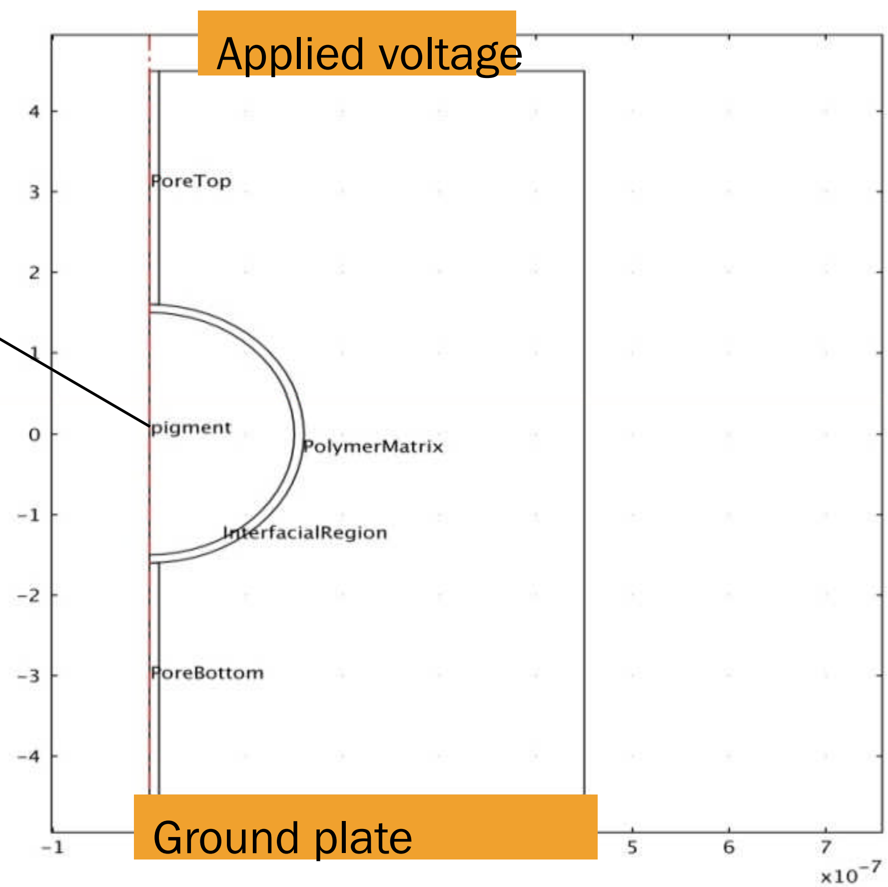
WHY DEVELOP MODELS OF COATING SYSTEMS?

- Physically based equations/models allow:
  - Extrapolation (Lifetime prediction)
  - Understanding of processes impacting measurement (Occam's razor) – **enhanced/optimized design**
  - Troubleshooting and new technology evaluation
  - Compare various accelerated weathering standards with various service environments
    - Predicting service life and property changes with time
    - Develop more realistic/representative accelerated tests
    - Gain insights into degradation mechanisms

Modeling allows testing hypothesis that are difficult or impossible to do experimentally.

SIMULATION





- Take pigment particle size and number
- Divide coating binder into average coverage